

On the Ionic Solubility-product.

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The theory of a constant ionic solubility-product was first advanced by Nernst,* from the analogy of the laws governing dissociation in gases. According to the principle of mass action, if the dissociation pressure of a system in equilibrium be changed by the introduction of an excess of either of the dissociated gases, combination takes place between them until equilibrium is restored. Thus, on the addition of either NH_3 or HCl to a system consisting of ammonium chloride in equilibrium with its dissociation products, ammonium chloride is produced. For each temperature, the product of the pressures of NH_3 and HCl is a constant. Similarly, Nernst found that the solubility of an electrolyte in water was reduced by the addition of any salt containing a common ion. The variations in the solubility of silver acetate (a sparingly soluble salt) in water containing known amounts of silver nitrate or sodium acetate were investigated, and the results obtained confirmed the view that a corresponding equilibrium law was here applicable. If we confine ourselves to substances of the simplest type RX , the law may be stated thus: "At a given temperature the solubility of a sparingly soluble electrolyte is dependent upon a constant, which is proportional to the product of the concentrations of the ions of the electrolyte."

The fundamental assumption made in the application of this law is that in a saturated solution of an electrolyte the undissociated salt in solution plays the part of an intermediary between the ions and the solid, being in equilibrium with the ions on the one hand and with the solid on the other. Consequently, so long as the solvent remains the same, the concentration of the undissociated salt is constant, however much the ionic concentrations may be separately varied by the introduction of other electrolytes; and the product of these ionic concentrations is also a constant.

Expressed algebraically, if s be the concentration of the saturated solution and m the degree of dissociation, m^2s^2 represents the solubility-product, and $(1-m)s$ the "constant undissociated value." These are connected, by the law of mass action, through the equation

$$m^2s^2 = (1-m)s \cdot c,$$

where c is the dissociation constant.

* 'Zeits. physikal. Chem.,' 1889, vol. 4, p. 372.

The theoretical solubilities of two substances containing a common ion in the presence of each other in aqueous solution, may now be established. Let a^2 and b^2 be their solubility-products, x and y their ionic concentrations in simultaneous solution. Then we have

$$x(x+y) = a^2, \quad y(x+y) = b^2,$$

$(x+y)$ being the concentration of the common ion. From this quadratic x and y are at once obtained.

If one of the substances is present not as a solid, but as a solution in water of known concentration s , the equations become

$$x(x+y) = a^2, \quad \frac{y(x+y)}{s-y} = c,$$

where c is the dissociation constant of the substance in solution. From these equations a cubic results, whence x and y are obtainable by trial.

In the above equations Ostwald's dilution law has been assumed, namely, that c is a constant for each particular electrolyte. This is true only in the case of weak acids and bases; for the majority of substances, the strong electrolytes, c is not constant, but increases with increase of concentration. Thus, with increase of concentration, the ratio of the ionised to the total substance dissolved becomes greater than the theoretical. The values of c for such a substance, however, can be determined for each concentration, and the value at saturation used to find the solubility-product. Noyes,* indeed, has used the values thus found not only for solubility determinations such as are indicated above, but also for the reverse problem of determining the degree of dissociation of a second substance by the solubility method.

The above assumption of a constant undissociated value has been attacked both theoretically and experimentally by Arrhenius.† Arrhenius showed that the assumption has no sound theoretical basis, and on determining the solubilities of silver salts of certain organic acids in water and in aqueous solutions containing excess of the corresponding sodium salts, he found that the undissociated value was not constant, but decreased with increase of concentration.

These results of Arrhenius have been investigated by Stieglitz.‡ Stieglitz, comparing this decrease of the undissociated part with the ratio of the ionic to the total strength, which, as mentioned above, increases beyond theoretical with increase of concentration, has formulated the hypothesis that the two

* 'Zeits. physikal. Chem.,' 1892, vol. 9, p. 603.

† 'Zeits. physikal. Chem.,' 1899, vol. 31, p. 197.

‡ 'Journ. Amer. Chem. Soc.,' 1908, vol. 30, p. 946.

effects counterbalance each other, and consequently restates the theory of the constant solubility-product in an empirical form. But the results of Arrhenius, as worked out in the above paper, give divergences in the solubility-product of from 5 to 10 per cent., and so long as such divergences exist unexplained, the theory can hardly be regarded as even empirically established; it remains no more than an approximation.

Previous investigations upon the simultaneous solubilities in water of two substances containing a common ion have been confined to those cases in which the substances examined have been of the same type, *i.e.* either both strong or both weak electrolytes. The case of two strong electrolytes has been most frequently examined, the special interest here lying in the question whether the law of mass action is, or is not, applicable. Fewer instances of the simpler case of two weak electrolytes have been investigated, but, in both types, the hypothesis of the constancy of the solubility-product has been considered to give results consistent with those obtained experimentally, although, even in dilute solutions, the agreement is only approximate. For instance, in a solution saturated simultaneously with thallium chloride and thallium bromate, the product of the ionic concentrations of each was found to be increased by about 5 per cent.* The saturated solutions of each of the above salts are (approximately) only one-fortieth normal.

No experiments, however, have been made with two substances of opposite types—one strong and one weak electrolyte—and the primary object of the following research was to supply this deficiency. Here also arises the question of the applicability of the law of mass action. In preliminary experiments divergences from the theoretical result of several per cent. were obtained, similar to that given above. In parallel experiments on the two types already investigated even larger differences were observed, far exceeding the limits of experimental error. Finally a series of experiments on all the possible types of combination of two electrolytes was carried out, first with dilute and afterwards with more concentrated solutions, in order to ascertain the cause of these divergences, and more especially to discover whether they formed an inherent defect in the theory or could be explained away on other grounds.

EXPERIMENTAL.

The substances used were acids of the simple type HX. Weak electrolytes: salicylic acid, $C_6H_4(OH).COOH$; ortho-nitrobenzoic acid, $C_6H_4(NO_2).COOH$; hippuric acid, $NH(CO.C_6H_5).CH_2.COOH$; formic acid,

* A. A. Noyes, 'Reports of Congress of Arts and Sciences, St. Louis,' vol. 4, p. 322.

H.COOH; acetic acid, CH_3COOH ; and malonic acid, $\text{CH}_2(\text{COOH})_2$. (The last named was used only in such concentrations as allowed it to be considered as a monobasic acid, splitting up into the ions $\text{CH}_2\begin{matrix} \text{COO}' \\ \text{COOH} \end{matrix}$ and $\text{H}\cdot$).

Strong electrolytes: hydrochloric acid; picric acid, $\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3$; and trinitrometacresol or methyl picric acid, 1:3:2:4:6- $\text{C}_6\text{H}(\text{CH}_3)(\text{OH})(\text{NO}_2)_3$.

The solid acids were purified by recrystallisation from freshly-distilled water; small crystals suitable for the experiments being obtained by rapid cooling from a hot saturated solution. Samples tested gave sharp and distinct melting points. The liquid acids were purified by distilling, and rejecting the first and last portions of the distillate. In all cases solutions were made up with freshly-distilled water, and the glass vessels employed were well steamed out before first using.

The concentrations of the saturated solutions of certain of the above acids at 25°C . were first determined. A few grammes of the acid were placed in a glass-stoppered bottle, half filled with water; over the neck of the bottle a square of rubber sheeting was tied tightly, and the bottle was then clamped in the stirrer of a thermostat and rotated for several days. A measured quantity (25 to 100 c.c., according to the strength of the solution) was then removed by means of a pipette, the body of the bottle remaining in the thermostat. To the end of the pipette was fitted a filter-cover, to prevent the entrance of any crystals, and the pipette itself, when not in use, was kept in a glass tube immersed in the thermostat, so that it was at the same temperature as the solution, and no crystallising occurred inside it. The solution was titrated immediately against baryta, phenolphthalein being used as an indicator. The bottle was again circulated in the bath, and the solution tested every few days until a steady value was reached.

Another method, used for single acids only, was to make a saturated solution above 25°C ., add a nucleus of crystals, and rotate in the thermostat as before until a constant titre was obtained. The true concentration of the saturated solution at 25°C . was thus approached from both directions.

Limits of Error.—The above experiments were performed in duplicate; divergences rarely exceeded 0.2 per cent., and were never greater than 0.4 per cent. The two methods also gave results agreeing well within this limit.

The temperature of the thermostat was maintained within 0.1°C . of 25°C . The thermostat being very large, any change of temperature was correspondingly slow.

The baryta solution used, approximately 1/40 normal, was standardised against each of the acids. The different values obtained varied by less than 0·2 per cent. This, besides testifying to the purity of the acids used, allowed the employment of one mean value, greatly simplifying the calculations in subsequent experiments. With picric and methyl picric acids, the end point was at first difficult to distinguish, owing to the disturbing colour effect, but after some practice the first permanent change of tint could be detected quite accurately by using a comparison solution.

In most cases the saturation point was soon reached; methyl picric acid, however, attained its full value only after two months, picric acid not even then. It was found that the presence of a few drops of ligroin or benzene in the solution shortened the necessary time for methyl picric to a few days, but the end points reached differed from that obtained with pure water. Ligroin, in which the acid is moderately soluble, increased its solubility by 2 per cent.; benzene, in which it is freely soluble, by 6 per cent. A considerable difference was thus caused by the presence of the extremely small amounts of each in solution in the water. This is noteworthy in view of results afterwards obtained.

In Table I below the concentrations of the saturated solutions of the acids are given in normalities; from these, by means of the dissociation constant, the solubility-product and the "constant undissociated value" of each acid are obtained.

Table I.—Solubilities of Single Acids.

Acid.	Solubility.	Solubility product.	"Constant undissociated value."
Salicylic	0·01634 N	0·0000130	0·01273 N
<i>o</i> -nitrobenzoic	0·04360 N	0·0001849	0·03000 N
Methyl picric	0·01000 N	0·0000846	0·00080 N
„ (ligroin present)	0·01019 N	—	—
„ (benzene present)	0·01059 N	—	—
Hippuric	0·02048 N	0·0000041	0·01846 N

The following dissociation constants* were used above, and in calculating the theoretical results of subsequent experiments:—

Salicylic acid.....	0·00102	Formic acid.....	0·000214	Hippuric acid...	0·000222
<i>o</i> -Nitrobenzoic acid	0·00616	Malonic acid ...	0·00158		

It was necessary to determine specially the values given above in the case of methyl picric acid, since the molecular conductivities of the acid and of its sodium salt had not been previously tabulated.

* Ostwald, 'Zeits. physikal. Chem.,' 1889, vol. 3, p. 418.

Molecular Conductivity of Methyl Picric Acid.

The sodium salt was first obtained by adding the requisite volume of sodium hydroxide solution (freshly prepared from metallic sodium and standardised by methyl picric acid) to a known weight of methyl picric acid. On evaporating the liquid to small bulk crystals were obtained, which were recrystallised from water and alcohol. Sodium picrate was also prepared by a similar method.

The values for the molecular conductivities obtained from these salts, however, were obviously too low. The salts were finally found to consist of a hydrate, the water from which could not be expelled under 100° C. Owing to their explosive nature it was inadvisable to heat the salts above this temperature.

By neutralisation, as before, and then direct addition of the requisite volume of water to bring the solution to N/32, solutions were obtained giving the following values for the molecular conductivity. Those for sodium picrate, given for comparison, are practically identical with Ostwald's values for that salt.*

<i>v.</i>	Sodium picrate.	Sodium methyl picrate.
32	72·9	71·3
64	76·1	73·4
128	78·1	75·2
256	79·7	76·9
512	81·2	78·6
1024	82·6	80·0
Whence—		
∞	85·7	83·1

The above results are the mean values of two determinations. Taking the values $\text{Na} = 51\cdot0$, $\text{H} = 349\cdot5$ (the mean of the values given by Ostwald and Kohlrausch), we obtain, for the maximum molecular conductivities of the acids, the values 384·2 and 381·6 respectively.

The molecular conductivities of the acids themselves were then determined, and are given below, together with the values of the degree of dissociation (m) obtained therefrom:—

<i>v.</i>	Picric acid.	<i>m.</i>	Methyl picric acid.	<i>m.</i>
32	343·4	0·894	—	—
64	354·9	0·924	—	—
128	360·7	0·939	352·9	0·925
∞	384·2	1·0	381·6	1·0

* 'Allg. Chemie,' 1893, vol. 2, p. 751.

By drawing the curves of the values of m given above we obtain, by extrapolation, for N/100 methyl picric acid (the saturated strength at 25° C.) the value $m = 0.92$. From this the solubility product and the "constant undissociated value" are obtained.

The above values for the molecular conductivities of the acids are in general agreement with those given for picric acid by Ostwald* and Rothmund;† but the degree of error may be fully 1 per cent. This would affect the degree of dissociation to the same extent; but, by trial from the equations, it was found that an error of 5 per cent. was required to affect the solubility determinations, afterwards made with the acids, beyond the limits of experimental error.

The conductivities were determined with a rotating commutator and galvanometer, more satisfactory results being obtained with this apparatus than with the usual induction coil and telephone, especially for the more dilute solutions.

In the determination of the solubility of one acid in the presence of another, the method of procedure was exactly similar to that already described for single acids. The experiments were of two classes: in the first, two solid acids were taken with water; in the second, one acid was present as a solid, the other as a solution in water of known strength. In all cases the end point was quickly reached, even methyl picric, in the presence of another acid, attaining the steady state in a few days.

The first investigations were of the simplest type, the two acids obeying Ostwald's dilution law. Of these, salicylic and *o*-nitrobenzoic acids are good examples, and a full series of experiments with these two acids was carried out, the results of which are shown in Table II (p. 207). Since they serve to illustrate the other cases, they are commented upon in detail.

It will be seen that the amount of acid in solution is in every case in excess of the theoretical. The divergences in Sections B and C increase with the strength of the original solution taken, and the greatest divergence is obtained in Section A, where both acids are present in the solid form. All the differences are far beyond the limits of experimental error.

There are, however, some small corrections to be made in the above figures. The results are given in normalities, whereas to be strictly comparable they should be expressed in gramme-molecules in 100 gm. of water. But this correction, instead of explaining the divergences, only increases them, for, as the solutions become more concentrated, the ratio of the weight of water present to the total weight becomes less, and the correction is thus a positive

* 'Zeits. physikal. Chem.,' 1887, vol. 1, p. 77.

† *Ibid.*, 1903, vol. 46, p. 845.

Table II.—Salicylic and *o*-Nitrobenzoic Acids.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergences.
A. Solid salicylic	Salicylic = 0·01365 N		
Solid <i>o</i> -nitrobenzoic	<i>o</i> -Nitrobenzoic = 0·04314 N		
	0·05679 N	0·05843 N	+ 0·00164 N
B. Known solution salicylic, Solid <i>o</i> -nitrobenzoic—			
(a) Salicylic = 0·00937 N	<i>o</i> -Nitrobenzoic 0·04328 N	0·04357 N	+ 0·00029 N
(b) „ = 0·01356 N	0·04316 N	0·04402 N	+ 0·00086 N
(c) „ = 0·01624 N	0·04301 N	0·04413 N	+ 0·00112 N
C. Known solution <i>o</i> -nitrobenzoic, Solid salicylic—			
(a) <i>o</i> -Nitrobenzoic = 0·01565 N	Salicylic 0·01430 N	0·01447 N	+ 0·00017 N
(b) „ = 0·04310 N	0·01366 N	0·01445 N	+ 0·00079 N
(c) „ = 0·04358 N	0·01365 N	0·01439 N	+ 0·00074 N

one, and also increases with concentration. There must also be taken into account the increase of the density of the solution with concentration; this entails a smaller negative correction. The final correction is, therefore, small and positive, in most cases well within the limits of experimental error, and so does not materially affect the results. Density determinations, however, were always made, and in the table below a typical example of the correction is given. Another case is shown after Table III; all other tables give results in normalities only.

Corrections for Density, etc.

The corrections for Section B of Table II are here given. Densities were obtained by means of a 25 c.c. pipette and a weighing bottle, and are liable to an error of 0·0002.

Strength of salicylic acid solution taken.	Density.	Final strength (salicylic and <i>o</i> -nitrobenzoic acids).	Density.
—	0·9963	0·04360 N	0·9998
0·00937 N	0·9968	0·05294 N	1·0001
0·01356 N	0·9970	0·05758 N	1·0009
0·01624 N	0·9973	0·06037 N	1·0012

When we express these strengths in gramme-molecules per 100 grm. of water, we obtain the following values. The last column shows the correction necessary to transfer results in normalities to correct results. (For obtaining, however, the “effective” part of this correction, it is necessary to subtract the initial value of it from its value at the given concentration. An example is given below.)

Strength of salicylic solution.	Total titre.	<i>o</i> -Nitrobenzoic dissolved.	Correction.
—	0·04392	0·04392	+ 0·00032
0·00941	0·05340	0·04399	+ 0·00042
0·01362	0·05810	0·04448	+ 0·00046
0·01632	0·06093	0·04461	+ 0·00048

The "effective" correction is thus, even in the last case, only $(0·00048 - 0·00032) = 0·00016$. This is less than 0·3 per cent. of the whole titre.

In Sections B and C of Table II it will be seen that not only does the divergence from theory increase with increase of concentration, but that the actual amount of acid dissolved, instead of decreasing, at first rapidly and then more slowly, as demanded by the theory, either shows an increase or becomes practically constant. The divergences from theory are therefore fundamental. The result of another experiment will show this more clearly. A saturated solution of *o*-nitrobenzoic acid, of strength 0·04358 N, free from solid, was added to solid salicylic acid and shaken in the thermostat until constant. The strength was now 0·05797 N. Since the concentration of the hydrogen ion had been increased, the solution should be supersaturated with respect to *o*-nitrobenzoic acid. But on adding solid *o*-nitrobenzoic acid to the solution, and shaking again until the titre was constant, the concentration rose to 0·05845 N, *i.e.* the solution was not supersaturated, but unsaturated.

A comparison of the three results of Sections A, B (*b*), and C (*b*) is interesting. The concentrations of the solutions originally taken in B (*b*) and C (*b*) are, as nearly as possible, those shown by A to be theoretically saturated in presence of the other acid. The final titre should therefore be the same in all three cases. Instead of the theoretical value of 0·05679 N, however, the three values obtained are 0·05843 N, 0·05758 N, and 0·05755 N respectively, which differ widely not only from the theoretical value but also from each other. The presence of solid acid allows an excess beyond theory to be dissolved; this is allowed in the case of both acids in A, in the case of *o*-nitrobenzoic only in B (*b*), and in the case of salicylic only in C (*b*). Hence we may expect the divergence in A to be equal, as a first approximation, to the sum of the divergences in B (*b*) and C (*b*). The experimental results are 0·00164 N and $(0·00086 \text{ N} + 0·00079 \text{ N}) = 0·00165 \text{ N}$. (See Table II.)

In Sections B (*c*) and C (*c*) saturated solutions (free from solid) of the one acid were taken, and treated with the other solid. Further consideration

of the results is left over until the remaining experiments on this and other types are given.

The results of other experiments with two weak acids are given in Table III, which shows the solubilities of salicylic and *o*-nitrobenzoic acids in known solutions of formic and malonic acids. In all cases the differences from theory are small and negative, but by making the corrections for density, etc., such differences are either destroyed or converted into small positive divergences, in all cases within error limits of the theoretical result. A typical series of corrections is given in Table IIIA.

Table III.—Remaining Experiments with Two Weak Acids.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergences.
A. Known solutions formic,			
Solid salicylic—			
(a) Formic = 0·05168 N	Salicylic 0·01539 N	0·01531 N	−0·00008 N
(b) „ = 0·09977 N	0·01496 N	0·01474 N	−0·00022 N
B. Known solutions formic,			
Solid <i>o</i> -nitrobenzoic—			
(a) Formic = 0·05168 N	<i>o</i> -Nitrobenzoic 0·04320 N	0·04304 N	−0·00016 N
(b) „ = 0·09977 N	0·04289 N	0·04266 N	−0·00023 N
C. Known solutions malonic,			
Solid salicylic—			
(a) Malonic = 0·03126 N	Salicylic 0·01502 N	0·01485 N	−0·00017 N
(b) „ = 0·10088 N	0·01417 N	0·01408 N	−0·00009 N
(c) „ = 0·20036 N	0·01378 N	0·01362 N	−0·00016 N
D. Known solutions malonic,			
Solid <i>o</i> -nitrobenzoic—			
(a) Malonic = 0·03126 N	<i>o</i> -Nitrobenzoic 0·04285 N	0·04279 N	−0·00006 N
(b) „ = 0·10088 N	0·04159 N	0·04153 N	−0·00006 N
(c) „ = 0·20036 N	0·03992 N	0·03967 N	−0·00025 N

Table IIIA.—Corrections for Density, etc.

Known solutions formic acid } (see Table III, Section A).
Solid salicylic acid

Strength of formic acid solution taken.	Density.	Final strength (formic and salicylic acids).	Density.
—	0·9963	0·01634 N	0·9973
0·05168 N	0·9966	0·06699 N	0·9976
0·09977 N	0·9969	0·11451 N	0·9978

Expressing these strengths in gramme-molecules per 100 grm. water, we have :—

Strength of formic solution.	Total titre.	Salicylic dissolved.	Correction.
—	0·01642	0·01642	+0·00008
0·05198	0·06745	0·01547	+0·00016
0·10054	0·11553	0·01499	+0·00025

The "effective" correction is only $(0·00025 - 0·00008) = 0·00017$ at the greatest concentration. This is less than 0·2 per cent. of the whole titre.

In the next table there are given the results of experiments with two strong acids. For the calculation of the theoretical results the following table of dissociation values for hydrochloric acid was used:—

$$\begin{array}{cccc} v = & 16 & 32 & 64 & 128, \\ m = & 0·935 & 0·953 & 0·966 & 0·972. \end{array}$$

The dissociation values of picric and methyl picric acids at various dilutions have already been given.

Table IV.—Experiments with Two Strong Acids.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergences.
A. Known solutions hydrochloric, Solid methyl picric—	Methyl picric		
(a) Hydrochloric = 0·00895 N	0·00669 N	0·00641 N	−0·00028 N
(b) „ = 0·01593 N	0·00510 N	0·00487 N	−0·00023 N
B. Known solution picric acid, Solid methyl picric—	Methyl picric		
(a) Picric acid = 0·01013 N	0·00651 N	0·00702 N	+0·00051 N

Here also divergences from theoretical results are obtained; negative in the case of methyl picric and hydrochloric, positive in the case of methyl picric and picric acids.

Table V gives examples of weak acids (salicylic and *o*-nitrobenzoic) dissolved in known solutions of a strong acid (hydrochloric). The divergences are pronounced, and in the negative direction. In the example A (*b*) it will be seen that the decrease is large enough, although the hydrochloric acid solution is only one-thirtieth normal (rather more than a gramme per litre), to bring the total amount of salicylic acid dissolved below its "constant undissociated value." A corresponding result was obtained by Arrhenius (*loc. cit.*) only with more concentrated solutions of two strong electrolytes.

Table V.—Weak Acids in Hydrochloric Acid Solutions.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergences.
A. Known solutions hydrochloric, Solid salicylic acid—			
(a) Hydrochloric = 0·01786 N	Salicylic 0·01345 N	0·01290 N	—0·00055 N
(b) „ = 0·03573 N	0·01310 N	0·01238 N	—0·00072 N
B. Known solutions hydrochloric, Solid <i>o</i> -nitrobenzoic acid—			
(a) Hydrochloric = 0·01786 N	<i>o</i> -Nitrobenzoic 0·03753 N	0·03681 N	—0·00072 N
(b) „ = 0·03573 N	0·03478 N	0·03390 N	—0·00088 N

Table VI below completes the series by giving those cases in which a strong acid (methyl picric) was dissolved in known solutions of weak acids (salicylic and *o*-nitrobenzoic). In the case of methyl picric and salicylic acids a full investigation was made, similar to that carried out with salicylic and *o*-nitrobenzoic acids.

Table VI.—Methyl Picric Acid and Weak Acids.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergences.
A. Known solution <i>o</i> -nitrobenzoic, Solid methyl picric acid— (a) <i>o</i> -nitrobenzoic = 0·01975 N			
	Methyl picric 0·00736 N	0·00800 N	+0·00066 N
B. Solid salicylic acid Solid methyl picric acid			
	Salicylic = 0·01404 N Methyl picric = 0·00935 N		
	0·02339 N	0·02613 N	+0·00274 N
C. Known solutions salicylic acid, Solid methyl picric acid— (a) Salicylic = 0·00981 N (b) „ = 0·01393 N			
	Methyl picric 0·00955 N	0·01063 N	+0·00108 N
	0·00935 N	0·01072 N	+0·00137 N
D. Known solution methyl picric, Solid salicylic acid— (a) Methyl picric = 0·00938 N			
	Salicylic 0·01404 N	0·01532 N	+0·00128 N

The results of sections B, C (b), and D may be compared. In the two latter the strengths of the original solutions are those shown by B to be theoretically saturated in presence of the other acid. (Compare Table II.) The divergence in B may be expected to be equal to the sum of the other two divergences, to a first approximation. The experimental results are 0·00274 N and (0·00137 N + 0·00128 N) = 0·00265 N.

The differences in Table VI are all large and positive. It will be seen that methyl picric acid is more soluble in salicylic acid solutions than in pure water.

In none of the above tables is the theory exactly followed, and a further experiment was performed, to ascertain whether the divergences obtained were superposable. A known solution of hydrochloric acid was taken, and two weak acids (salicylic and *o*-nitrobenzoic acids) added. The differences to be expected from theory were estimated by interpolation from the results of the preceding tables, and compared with the difference experimentally obtained.

Table VII.—Two Weak Acids in Hydrochloric Acid Solution.

Initial state.	Acid dissolved (theory).	Acid dissolved (expt.).	Divergence.
Known hydrochloric acid solution, Solid salicylic acid, ,, <i>o</i> -nitrobenzoic acid— (a) Hydrochloric = 0·02957 N...	Salicylic = 0·01316 N <i>o</i> -Nitrobenzoic = 0·03608 N 0·04924 N	0·04935 N	+ 0·00011 N

The following divergences were to be expected (see Tables II and V):—

- (a) Due to solid salicylic and solution of *o*-nitrobenzoic + 0·0006 N.
- (b) Due to solid *o*-nitrobenzoic and solution of salicylic + 0·0008 N.
- (c) Due to solid salicylic and solution of hydrochloric — 0·0006 N.
- (d) Due to solid *o*-nitrobenzoic and solution of hydrochloric — 0·0008 N.

The solution should therefore be approximately of theoretical strength if the various differences are superposable. Seeing that the accuracy of a large number of experiments is involved in the values of the expected divergences given above, the experimental result agrees with this supposition well within the limits of error.

A general consideration of the results in Tables II to VII shows that the theory holds strictly in none of the possible combinations of acids. It makes no difference whether they are both weak, both strong, or one of each type; similar divergences of several per cent. are obtained in every case. And these divergences, though usually numerically small, are fundamental in each direction; the upper limit consistent with the theory—the total solubility in pure water—and the lower limit—the “constant undissociated value”—are both passed in very dilute solutions.

Now, on an examination of the tables, the following rule appears to hold:

that an increase beyond theoretical is obtained when two acids chemically similar (*i.e.*, salicylic and *o*-nitrobenzoic) are present in solution, and a decrease when two acids chemically dissimilar (*i.e.*, salicylic and hydrochloric) are present. This rule seems to be quite general, and not dependent at all upon the types of the two acids. In Table III the two acids are of neither very similar nor very dissimilar character, and the divergences obtained are but slight, and within error limits of the theoretical. There may be an increase or a decrease, but, at the concentrations tested, it is too small a percentage of the total titre to be perceived.

The fact that a solution of one acid can dissolve more of a chemically similar acid than theory demands, leads to the inquiry whether the ionic effect of the acids upon each other is not also accompanied by a solvent effect. The small quantity of the first acid in solution might, by its solvent action upon the second acid, cause an appreciable increase in the result. That the cause is quite adequate may be seen from the relatively large increase in the solubility of methyl picric acid in water in the presence of small quantities of ligroin or benzene dissolved in the water, as before described. A decrease below the theoretical result would be accounted for, under this view, by the comparative insolubility of the two acids in each other.

The divergence from theory would thus steadily increase with increase of concentration, and this is actually the case. Stronger confirmation, however, is given to the hypothesis by the results of the two series of experiments carried out with salicylic and *o*-nitrobenzoic acids, and with salicylic and methyl picric acids, respectively. When both acids are present in the solid form, both exert a solvent effect, and this is, to a first approximation, found to be the sum of their two separate solvent effects, determined by suppressing the solid form of one acid, and having it present instead as a solution, theoretically saturated in the presence of the other acid.

To test the above view further it is necessary to perform a series of experiments with one solid and one liquid acid, the solubility of the solid acid in the liquid one being either much greater or much less than its solubility in pure water. From the solubility results obtained by treating the solid acid with known solutions of the liquid acid in water it can then be seen whether the increase or decrease from theory is capable of being accounted for in this way.

The case of salicylic or *o*-nitrobenzoic with formic acid is a good example, both solids being much more soluble in formic acid than in water. The above, however, were the only cases in which no definite increase or decrease from theoretical was observed, the error limit obscuring the result at the concentrations tested.

Another series of experiments was therefore carried out with more concentrated solutions, both in the above and in other cases. The method of estimating volumetrically with baryta here became impracticable, owing to the overwhelming concentration of the solvent acid compared with that of the acid dissolved, in which latter small variations were consequently impossible to measure.

The method employed was that of evaporation. The solutions were prepared in the same manner as already described, 25 c.c. of the liquid were pipetted out into a weighed evaporating dish, and evaporated down to dryness. The amount of the dissolved solid was then found by weighing, and its titre in the solution directly calculated. The cases investigated were :—

- (a) In solutions of formic acid : Salicylic acid, hippuric acid.
- (b) In solutions of acetic acid : Salicylic acid.
- (c) In solutions of hydrochloric : Salicylic acid, *o*-nitrobenzoic acid.

Solutions containing hippuric acid could be evaporated down on the steam-bath without loss of solid by volatilisation; those containing salicylic and *o*-nitrobenzoic acids, since these proved to be more or less volatile with steam, were allowed to evaporate slowly at the ordinary temperature.

The residues obtained weighed from 0.1 to 0.04 of a gramme; the error limit in the latter case is about 1 per cent. Experiments performed in duplicate gave results agreeing together within this limit, and the results of this method, as tested with some of the more dilute solutions, were closely concordant with those obtained volumetrically.

The results obtained are shown in both tabular and graphic form. Some volumetric determinations are also given in the tables, both for the purpose of comparison with the gravimetric results and for use in the accompanying curves.

Results are expressed, as before, in normalities. The corrections described in the volumetric determinations, although much larger here owing to the greater concentrations of the solutions used, are not applied. That due to density change is never so much as 1 per cent. of the total, and is therefore still within the limits of experimental error. That due to replacement of water by acid is as much as 10 per cent. of the total in the most concentrated solutions, but since we are here considering the solvent actions of both water and acid, it is preferable to compare solutions containing equal weights of total solvent than those containing equal weights of water, and such solutions are represented, within error limits, in the uncorrected figures below.

Table VIII.—Gravimetric Determinations.

A. Salicylic Acid in Solutions of Formic Acid. (See fig. p. 216.)

Strength of formic acid solution (per cent.).	Weight of residue from 25 c.c. (in grms.).	Strength of dissolved acid (gravimetrically).	Strength of dissolved acid (volumetrically).
0	0·0563	0·01631 N	0·01634 N
0·24	—	—	0·01531 N
0·46	—	—	0·01474 N
0·625	0·0512	0·01484 N	—
1·25	0·0516	0·01496 N	—
2·5	0·0530	0·01536 N	—
5	0·0592	0·01716 N	—
10	0·0725	0·02101 N	—

B. Hippuric Acid in Solutions of Formic Acid. (See fig.)

Strength of formic acid solution (per cent.).	Weight of residue from 25 c.c. (in grms.).	Strength of dissolved acid (gravimetrically).	Strength of dissolved acid (volumetrically).
0	0·0915	0·02045 N	0·02048 N
1·25	0·0901	0·02014 N	—
2·5	0·0930	0·02078 N	—
5	0·1018	0·02275 N	—
10	0·1191	0·02661 N	—

C. Salicylic Acid in Solutions of Acetic Acid. (See fig.)

Strength of acetic acid solution (per cent.).	Weight of residue from 25 c.c. (in grms.).	Strength of acid dissolved (gravimetrically).
0	0·0563	0·01631 N
0·625	0·0584	0·01691 N
1·25	0·0602	0·01745 N
2·5	0·0636	0·01846 N
5	0·0710	0·02059 N

D. Salicylic Acid in Solutions of Hydrochloric Acid. (See fig.)

Strength of hydrochloric acid solution.	Weight of residue from 25 c.c. (in grms.).	Strength of dissolved acid (gravimetrically).	Strength of dissolved acid (volumetrically).
—	0·0563	0·01631 N	0·01634 N
0·0179 N	—	—	0·01290 N
0·0357 N	—	—	0·01238 N
0·125 N	0·0419	0·01214 N	—
0·25 N	0·0412	0·01194 N	—
0·5 N	0·0387	0·01123 N	—

E. *o*-Nitrobenzoic Acid in Solutions of Hydrochloric Acid. (See fig.)

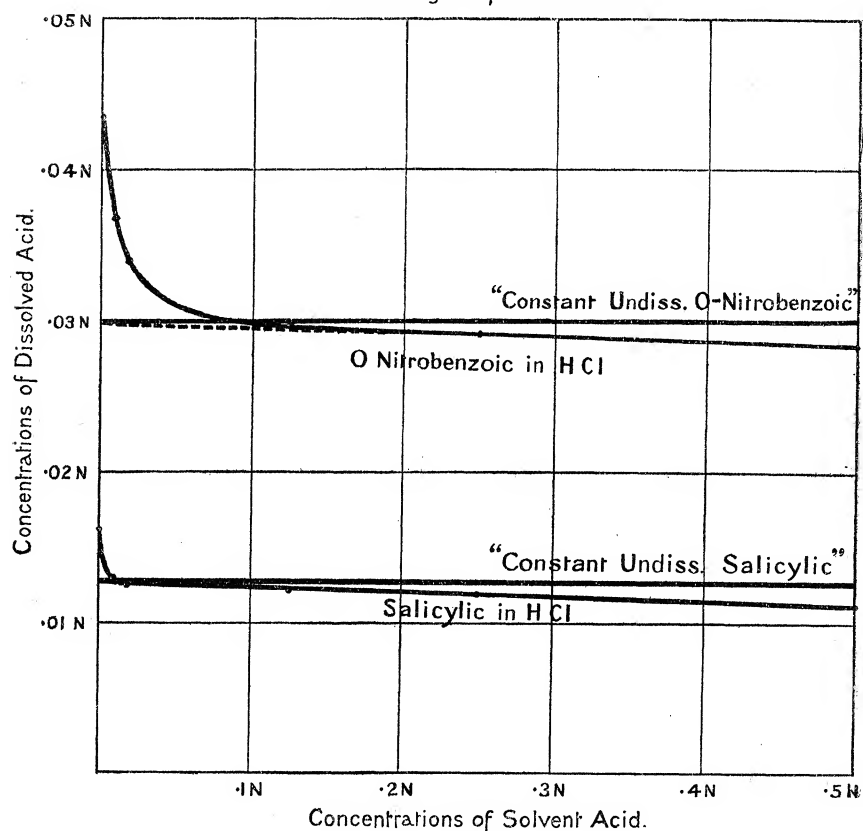
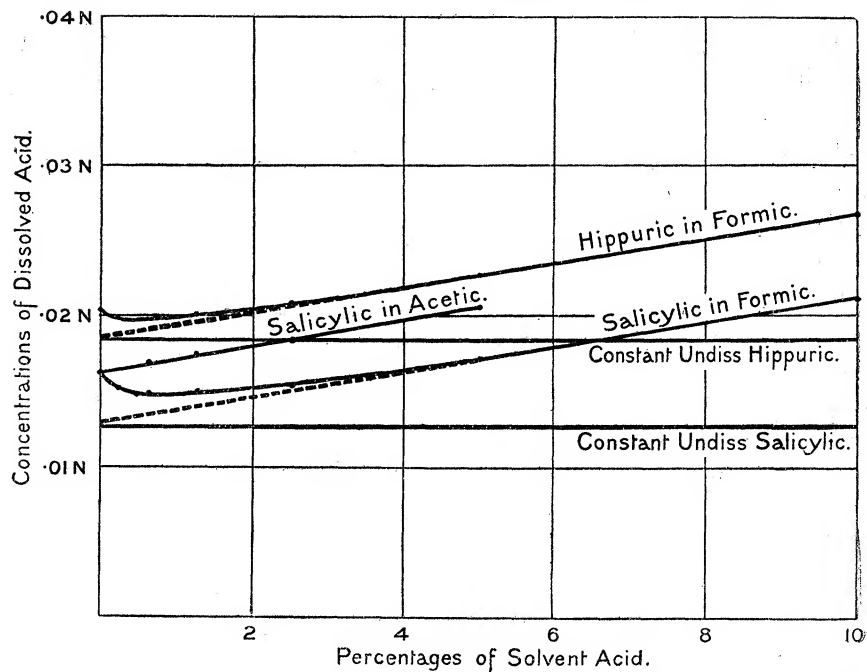
Strength of hydrochloric acid solution.	Weight of residue from 25 c.c. (in grms.).	Strength of dissolved acid (gravimetrically).	Strength of dissolved acid (volumetrically).
—	0.1804	0.04320 N	0.04360 N
0.0179 N	—	—	0.03681 N
0.0357 N	—	—	0.03390 N
0.125 N	0.1245	0.02980 N	—
0.25 N	0.1221	0.02922 N	—
0.5 N	0.1188	0.02846 N	—

The solubility curves obtained from the above table, as shown in the diagrams, consist of three types, according to the acid used as solvent. With solutions of acetic acid there is a continuous and regular increase in the solubility, with hydrochloric solutions a sharp initial decrease is obtained, followed by a much smaller and more regular decrease, while with formic acid solutions a small initial decrease is with increasing concentration soon converted into a regular increase.

The first case, that of acetic acid, may be considered as a case of pure solvent effect, for the degree of ionisation of the acid is so small that the ionic concentration could have, even in concentrated solutions, no measurable effect. The increase in solubility is proportional to the concentration of the acid in solution, and is quite regular as water is replaced in the solution by more solvent acid.

Formic acid is comparatively much stronger than acetic, and here it appears that the ionisation effect upon the acids employed is at first the more important, but the decrease in the solubility thus produced is soon neutralised, as the concentration increases, by the greater solvent power of the formic acid. The curve finally approximates to a straight line corresponding to the acetic acid type, showing a regular increase with increase of concentration. Thus there are two separate influences upon the solubility; an ionic effect proportionally large at first, but rapidly falling off with increase of concentration, and a solvent effect, directly proportional to the concentration.

With hydrochloric acid solutions the ionic effect is again considerably stronger than in the former case, and the solvent effect is negligible. A sharp drop, as the strength of the hydrochloric increases, carries the solubility of the acids used below the "constant undissociated value," and further decrease is very slow, being presumably due to the replacement of solvent water by non-solvent acid in the solution. In this case also the curve finally approximates to a straight line.



If these straight lines are produced backwards to meet the axis, it will be seen that they do so at or near the point of the so-called "constant undissociated value." (The only exception is in the case of salicylic in acetic acid, but this is practically a case of pure solubility.) Thus, if we consider these lines as dividing lines, we may regard the solubility of one acid in aqueous solutions of another as consisting of two portions:—

(a) An undissociated portion (below the line), increasing or decreasing regularly, according as the acid is more or less soluble in the solvent acid than in water.

(b) A dissociated portion (above the line), decreasing more or less rapidly according to the ionic strength of the solvent acid. This decrease is not regular, but is proportionally greater the less concentrated the solution is, falling off as the dissociated portion is suppressed by increase of concentration.

The solvent effect, acting directly upon the undissociated portion, will also indirectly affect the dissociated part of the substance in solution, since this must remain in equilibrium with the undissociated part. In the curves given, the acids exist in solution mainly in the undissociated state, hence this indirect effect is but small, and soon becomes negligible with increase of concentration, owing to the almost total suppression of the ionised part. In solutions of strong electrolytes, however, the indirect may be greater than the direct effect; hence the solubility curves in such cases will not finally approximate to straight lines which cut the axis, when produced backwards, at or very near to the "constant undissociated value." The case of salicylic acid in solutions of acetic acid is another example of the inapplicability of the rule in the event of the ionised portion persisting in appreciable quantity at all concentrations of the solvent acid.

The experimental divergences obtained from the values indicated by the theory of the constant solubility-product can thus be accounted for in all cases by this solvent effect. The divergences, positive or negative, are caused by the solvent influence of the two substances upon each other, and this, as shown in the above tables, is positive when the substances are chemically similar in character, negative when they are dissimilar. The amount of the divergence due to each acid can also, as in the case of salicylic and *o*-nitrobenzoic acids, be obtained to a first approximation.

The existence of this solvent effect renders it evident that the reverse problem, attempted by Noyes, of calculating the degree of dissociation of one substance by determining its solubilities in water and in a known solution of another substance containing a common ion, may sometimes lead to very erroneous results. In any case the results of such a

determination must be uncertain, since a wide variation in the assumed degree of dissociation corresponds in most instances to a very small change in the solubility, any decrease in undissociated substance dissolved being almost entirely balanced by an increase in dissociated, and *vice versa*. This fact explains also why, although the degrees of dissociation of the strong acids used in the above research are not yet accurately determined, being liable to an uncertainty of several per cent. in dilute solutions, the solubility results of other acids with them, as calculated from these values, are subject to a much smaller degree of error.

In conclusion, I have much pleasure in expressing my thanks to Prof. Walker, at whose suggestion and under whose direction the above research was carried out, for his advice and assistance during the whole period of its execution.

BAKERIAN LECTURE.—*A Chemically Active Modification of Nitrogen, Produced by the Electric Discharge.*

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[PLATE 8.]

§ 1. *Afterglow of Nitrogen.*

It is known that vacuum tubes frequently show a luminosity of the contained gas after discharge is over. In a previous paper* I was able to show that this effect, as it occurs in air, is of the nature of a phosphorescent combustion, and is due to the mutual reaction of nitric oxide and ozone, each formed in the discharge. In a second paper† it was shown that other phosphorescent combustions can be observed in ozone, notably of sulphur, sulphuretted hydrogen, acetylene, and iodine. Some of these give continuous spectra, but the majority band spectra.

In the first paper it was stated that pure nitrogen gives no afterglow whatever, and, with the simple induction coil discharge with which I was then working, this has been frequently verified since. Mr. Percival Lewis has, however, described an afterglow obtained in nitrogen when a jar

* 'Phys. Soc. Proc.,' Dec. 15, 1910, vol. 23, p. 66.

† *Ibid.*, Feb. 15, 1911, vol. 23, p. 147.